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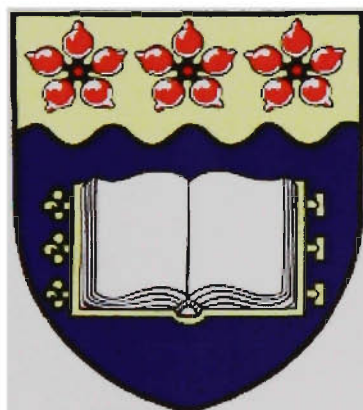
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Isotopic Characterisation of Atmospheric Nitrous Oxide by Fourier Transform Infrared Spectroscopy

A thesis submitted in fulfilment of the
requirements for the award of the degree

DOCTOR OF PHILOSOPHY

from



UNIVERSITY OF WOLLONGONG

by

FEDERICO TURATTI, BSc (Hons.)

Department of Chemistry, 2001

Certification

I, Federico Turatti, declare that this thesis, submitted in fulfilment of the requirements for the award of Doctor of Philosophy, in the Department of Chemistry, University of Wollongong, is wholly my own work unless otherwise referenced or acknowledged. The document has not been submitted for qualifications at any other academic institution.

Federico Turatti

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Publications

Sections of this work described in this thesis have been reported in the following publications:

- Turatti, F., D.W.T. Griffith, S.R. Wilson, M.B. Esler, T. Rahn, H. Zhang, and G.A. Blake, Positionally dependent ^{15}N fractionation factors in the photolysis of N_2O determined by high resolution FTIR spectroscopy, *Geophysical Research Letters*, 27 (16), 2489-2492, 2000.
- Turatti, F., D.W.T. Griffith, S.R. Wilson, M.B. Esler, L.P. Steele, T. Rahn, and H. Zhang, Isotopic analysis of atmospheric N_2O by FTIR spectroscopy: ^{15}N , ^{18}O and ^{15}N positional dependence, in *Cape Grim Baseline Air Pollution Station Annual Meeting*, edited by N. Tindale, CSIRO Atmospheric Research, Aspendale, 1999.
- Esler, M.B., D.W.T. Griffith, F. Turatti, S.R. Wilson, and T. Rahn, N_2O concentration and flux measurements and complete isotope analysis using FTIR spectroscopy, *Chemosphere: Global Change Science*, 2, 445-454, 2000.
- Griffith, D.W.T., S.R. Wilson, F. Turatti, M.B. Esler, and I.M. Jamie, Isotopomeric Analysis of Environmental Trace Gases by FTIR spectrometry: N_2O , CH_4 , CO_2 and H_2O , in *1st International Symposium on Isotopomers*, edited by N. Yoshida, Yokohama, Japan, 2001.
- Wilson, S.R., D.W. Griffith, F. Turatti, and J. Menegazzo, Characterisation of agricultural N_2O emission sources using isotopic labelling studies, in *Cape Grim Baseline Air Pollution Station Annual Scientific Meeting*, edited by N. Tindale, and N. Derek, Aspendale, Vic, Australia, 2000.

Abstract

Nitrous oxide is the third most important anthropogenic greenhouse gas after CO₂ and CH₄ and contributes 6% of the total terrestrial radiative forcing due to greenhouse gases. It is closely involved in the depletion of stratospheric ozone by providing one of the main sources of NO radicals. Biological processes such as nitrification and denitrification are primarily responsible for N₂O production. Despite its importance and years of research, the estimates of the global size of N₂O sources and sinks remain highly uncertain, and its budget is not yet fully balanced.

Analysis of N₂O isotopes can aid in reducing the large uncertainties in source and sink estimates by providing information that is complementary to the N₂O mixing ratio. Analysis of the mean $\delta^{15}\text{N}$ and mean $\delta^{18}\text{O}$ has already lead to some insight on the N₂O budget. Until very recently the intramolecular ¹⁵N positional isotopes ¹⁴N¹⁵N¹⁶O and ¹⁵N¹⁴N¹⁶O were not measurable by any analytical technique. The intramolecular difference $\delta^{14}\text{N}^{15}\text{N}^{16}\text{O} - \delta^{15}\text{N}^{14}\text{N}^{16}\text{O}$ is an additional isotopic discriminator than the mean $\delta^{15}\text{N}$ alone, as it directly describes the processes forming the N-N bond in N₂O production processes such as nitrification and denitrification.

This thesis describes the development of a high resolution Fourier transform infrared technique for the measurement of the N₂O isotopomers ¹⁴N¹⁵N¹⁶O, ¹⁵N¹⁴N¹⁶O, ¹⁴N¹⁴N¹⁸O and ¹⁴N¹⁴N¹⁷O. The FTIR technique utilises 0.012 cm⁻¹ resolution FTIR spectroscopy, a 2.4 m optical pathlength, 120 mL sample cell, with precise control of sample temperature and pressure. The typical analytical precision of the ¹⁴N¹⁵N¹⁶O and ¹⁵N¹⁴N¹⁶O isotopomers is of the order of 1-2 ‰, and approximately 3-4 ‰ for the oxygen isotopomers ¹⁴N¹⁴N¹⁸O and ¹⁴N¹⁴N¹⁷O. Two independent chemometric multivariate analytical methods were developed for determination of high resolution N₂O spectra: multi-micro-window classical least squares, and non-linear least squares. The strengths and limitations of the FTIR technique are analysed and compared to those of the complementary isotope ratio mass spectrometry technique. The FTIR technique is analytically robust and serves as an independent and complementary technique to N₂O analysis by isotope ratio mass spectrometry.

The FTIR technique was used to analyse N₂O from several contexts. The isotopic fractionation factors in the laboratory photolysis of N₂O at three wavelengths were determined by analysis of the unphotolysed N₂O fraction. Samples of nitrous oxide were extracted from whole air at an urban location over the period of approximately one year and isotopically characterised. The emissions of N₂O from a pig effluent fertilised crop field have been isotopically characterised. In each of the three contexts, results are interpreted in relation to the processes involved.

TABLE OF CONTENTS

<i>CERTIFICATION</i>	<i>II</i>
<i>ACKNOWLEDGMENTS</i>	<i>III</i>
<i>PUBLICATIONS</i>	<i>IV</i>
<i>ABSTRACT</i>	<i>V</i>
CHAPTER 1 INTRODUCTION	1
1.1 THE SIGNIFICANCE OF ATMOSPHERIC N₂O	2
<i>1.1.1 THE ATMOSPHERIC RADIATIVE BALANCE</i>	<i>2</i>
<i>1.1.2 THE N₂O STRATOSPHERIC CHEMISTRY</i>	<i>5</i>
1.2 THE N₂O BUDGET	6
<i>1.2.1 NATURAL SOURCES</i>	<i>9</i>
<i>1.2.1.1 Oceans</i>	<i>9</i>
<i>1.2.1.2 Soils under natural vegetation</i>	<i>10</i>
<i>1.2.2 ANTHROPOGENIC SOURCES</i>	<i>10</i>
<i>1.2.2.1 Arable land</i>	<i>10</i>
<i>1.2.2.2 Animal excreta</i>	<i>11</i>
<i>1.2.2.3 Biomass burning</i>	<i>11</i>
<i>1.2.2.4 Industrial sources of N₂O</i>	<i>11</i>
<i>1.2.2.5 Tropical forest conversion</i>	<i>12</i>
<i>1.2.2.6 Other potential N₂O sources</i>	<i>12</i>
<i>1.2.3 SINKS</i>	<i>13</i>
1.3 THE ISOTOPOMERS OF N₂O.....	15
<i>1.3.1 BUDGET IMPLICATIONS OF N₂O ISOTOPOMER ANALYSIS</i>	<i>17</i>
<i>1.3.2 ISOTOPOMER EFFECTS OF NITRIFICATION AND DENITRIFICATION</i>	<i>18</i>
<i>1.3.2.1 The denitrification mechanism</i>	<i>20</i>
<i>1.3.2.2 Nitrification</i>	<i>22</i>
<i>1.3.2.3 Isotopic fractionation during sink processes</i>	<i>23</i>
1.4 GAS ISOTOPOMER MEASUREMENT METHODS.....	26
<i>1.4.1 ISOTOPE RATIO MASS SPECTROMETRY</i>	<i>26</i>
<i>1.4.2 OPTICAL EMISSION SPECTROSCOPY</i>	<i>29</i>
<i>1.4.3 TUNABLE DIODE LASER SPECTROSCOPY</i>	<i>31</i>
<i>1.4.4 FOURIER TRANSFORM INFRARED SPECTROSCOPY</i>	<i>32</i>
1.5 INTRODUCTION TO THIS WORK	33
1.6 REFERENCES.....	35
CHAPTER 2 EXPERIMENTAL I: INFRARED SPECTROSCOPY AND QUANTITATIVE SPECTRAL ANALYSIS.....	40

2.1 THE INFRARED SPECTRUM OF THE NITROUS OXIDE MOLECULE	40
2.1.1 THE ROTATIONAL ENERGY LEVELS OF N_2O	40
2.1.2 THE VIBRATIONAL SPECTRUM OF N_2O	41
2.1.3 THE INFRARED SPECTRUM OF N_2O	42
2.2 FOURIER TRANSFORM INFRARED (FTIR) SPECTROSCOPY	44
2.2.1 BASIC FTIR THEORY.....	46
2.2.2 SPECTRAL SIGNAL TO NOISE RATIO (SNR).....	49
2.3 CALCULATING SPECTRA FROM FIRST PRINCIPLES	50
2.4 CALCULATION OF SYNTHETIC SPECTRA WITH MALT.....	53
2.5 CLASSICAL LEAST SQUARES (CLS).....	56
2.5.1 THEORY.....	56
2.5.2 WINDOWS AND REGIONS	59
2.5.3 THE WEIGHTS FOR EACH MICRO-WINDOW	63
2.5.4 EFFECT OF THE WEIGHTS ON DETERMINATION PRECISION	66
2.5.5 THE CAUSES OF WEIGHT VARIATION AND SPECTRUM TO SPECTRUM VARIABILITY.....	69
2.6 NON-LINEAR LEAST SQUARES (NLLS).....	69
2.6.1 THEORY.....	70
2.6.2 THE NON-LINEAR LEAST SQUARES ALGORITHM.....	71
2.6.3 OPTIMUM FITTING REGIONS.....	73
2.6.4 THE ADVANTAGES OF NON-LINEAR LEAST SQUARES OVER CLASSICAL LEAST SQUARES	80
2.7 REFERENCES	82
 CHAPTER 3 EXPERIMENTAL II: HARDWARE, SAMPLE HANDLING AND MEASUREMENT PROCEDURES	 84
3.1 THE FTIR SPECTROMETER AND OPTICAL CONFIGURATION	84
3.2 SAMPLE HANDLING AND TEMPERATURE CONTROL	85
3.3 SAMPLE MEASUREMENT PROCEDURES	92
3.3.1 SAMPLE INTRODUCTION AND MEASUREMENT.....	92
3.3.2 MEASURING N_2O WORKING STANDARD AND EVACUATED CELL REFERENCE SPECTRA	93
3.4 SELECTION OF AN N_2O WORKING STANDARD	94
3.5 EXTRACTING N_2O FROM SOURCES	99

3.5.1 N_2O EXTRACTION	100
3.6 REFERENCES.....	101
CHAPTER 4 EXPERIMENTAL III: OPTIMAL SPECTROSCOPIC CONDITIONS, TECHNIQUE PRECISION AND LIMITATIONS	102
4.1 ESTIMATING THE OPTIMAL N_2O AMOUNT AND SPECTROSCOPIC CONDITIONS	102
4.2 VALIDATION OF THE THEORETICAL IDEAL CONDITIONS	106
4.3 THE THEORETICAL PRECISION LIMITS.....	107
4.4 EFFECT OF TEMPERATURE CHANGES ON δ DETERMINATION.....	110
4.5 EFFECT OF SAMPLE PRESSURE ON δ DETERMINATION	114
4.6 EFFECT OF LINE SHAPE VARIABILITY ON δ DETERMINATION	117
4.7 WHAT LIMITS THE ISOTOPOMER PRECISION?	120
4.8 A SUMMARY OF THE HIGH RESOLUTION FTIR METHOD CONDITIONS	121
4.9 REFERENCES.....	122
CHAPTER 5 RESULTS I: ISOTOPIC ENRICHMENT FACTORS FOR $^{14}N^{15}N^{16}O$, $^{15}N^{14}N^{16}O$, $^{14}N^{14}N^{18}O$ AND $^{14}N^{14}N^{17}O$ IN THE LABORATORY PHOTOLYSIS OF N_2O.....	123
5.1 INTRODUCTION	123
5.2 EXPERIMENTAL	125
5.3 RESULTS AND DISCUSSION	126
5.4 CONCLUSIONS.....	139

5.5 REFERENCES.....	139
 CHAPTER 6 RESULTS II: ISOTOPOMERIC CHARACTERISATION OF TROPOSPHERIC N₂O	
6.1 INTRODUCTION	141
6.2 EXPERIMENTAL	142
6.3 RESULTS AND INTERPRETATIONS.....	143
6.3.1 LOCAL AND LARGE SCALE WEATHER CONDITIONS	143
6.3.2 THE N ₂ O, CO ₂ , CH ₄ AND CO MIXING RATIOS.....	145
6.3.3 THE MEAN $\delta^{15}\text{N}$ RELATIVE TO ATMOSPHERIC N ₂	146
6.3.4 INDIVIDUAL ¹⁵ N ISOTOPOMERS AND THE INTRAMOLECULAR ¹⁵ N DIFFERENCE, δ^{456} - δ^{546}	153
6.3.5 THE OXYGEN ISOTOPOMERS, ¹⁴ N ¹⁴ N ¹⁸ O AND ¹⁴ N ¹⁴ N ¹⁷ O.....	157
6.3.6 ISOTOPOMER CORRELATION WITH LOCAL SCALE WEATHER CONDITIONS.....	159
6.4 SUMMARY AND CONCLUSIONS.....	160
6.5 REFERENCES.....	161
 CHAPTER 7 RESULTS III: ISOTOPIC CHARACTERISATION OF N₂O FROM PIG EFFLUENT FERTILISED CROP SOILS.....	
7.1 THE ROLE OF SOILS IN GLOBAL N₂O EMISSIONS	163
7.2 EXPERIMENTAL	164
7.2.1 SITE AND EXPERIMENT DESCRIPTION.....	164
7.2.2 EXTRACTION OF N ₂ O FROM SOIL GAS EMISSIONS.....	165
7.2.3 MEASURING THE N ₂ O FLUX AND ISOTOPIC COMPOSITION	170
7.3 RESULTS.....	172
7.3.1 FLUXES OF N ₂ O AND CO ₂	172
7.3.2 N ₂ O ISOTOPIC COMPOSITION.....	173
7.4 RESULT INTERPRETATION AND DISCUSSION	174
7.4.1 N ₂ O FLUXES	174
7.4.2 $\delta^{15}\text{N}$ OF N ₂ O FROM EXPERIMENT SITES	180
7.4.3 THE INTRAMOLECULAR ¹⁵ N DIFFERENCE: δ^{456} - δ^{546} AND THE INDIVIDUAL δ^{456} AND δ^{546}	185
7.4.4 THE OXYGEN ISOTOPOMERS.....	187

7.5 CONCLUSIONS	193
7.6 REFERENCES	195
 CHAPTER 8 CONCLUSIONS.....	198
8.1 FURTHER WORK ALREADY IN PROGRESS	201
8.2 FURTHER WORK.....	203
8.3 OVERALL CONCLUSION	204
8.4 REFERENCES	205
 APPENDIX A PROCEDURES AND PUBLICATIONS	206
A.1 PROCEDURE FOR DISMANTLING THE VACUUM LINE AND WHITE CELL	206
A.2 PROCEDURE FOR WASHING THE WHITE CELL.....	207
A.3 PROCEDURE FOR ATTACHING CaF ₂ WINDOW TO THE WHITE CELL	208
A.4 REASSEMBLY PROCEDURE.....	209
A.5 PUBLICATIONS	209

LIST OF FIGURES

FIGURE 1.1 A CONCEPTUAL MODEL OF NITRIFICATION AND DENITRIFICATION.....19

FIGURE 1.2 THE PARALLEL MECHANISM FOR DENITRIFICATION.....21

FIGURE 1.3 THE SEQUENTIAL MECHANISM FOR DENITRIFICATION21

FIGURE 1.4 SCHEMATIC DIAGRAM OF THE NITRIFICATION MECHANISM.....23

FIGURE 1.5 VERTICAL PROFILES OF δ^{546} - δ^{456} OF N₂O FROM FTIR BALLOON FLIGHTS AS DESCRIBED BY GRIFFITH ET AL. [2000]25

FIGURE 1.6 SCHEMATIC DIAGRAM OF AN ISOTOPE RATIO MASS SPECTROMETER OPTIMISED FOR MEASURING $\delta^{15}\text{N}$ [MULVANEY, 1993].....27

FIGURE 1.7 BASIC COMPONENTS OF AN OPTICAL EMISSION ^{15}N ANALYSER [PRESTON, 1993]30

FIGURE 1.8 SCHEMATIC DIAGRAM OF AN FTIR INSTRUMENT FOR ANALYSIS OF $\delta^{13}\text{C}$ AND TRACE GASES [ESLER ET AL., 2000A].....33

FIGURE 2.1 NORMAL VIBRATIONS AND THEIR FUNDAMENTAL FREQUENCIES FOR THE N₂O MOLECULE.41

FIGURE 2.2 SYNTHETICALLY CALCULATED FTIR SPECTRA BETWEEN 2120 AND 2280 cm^{-1} OF THE SIX MOST NATURALLY ABUNDANT N₂O ISOTOPOMERS.....44

FIGURE 2.3 SCHEMATIC DIAGRAM OF THE MICHELSON INTERFEROMETER45

FIGURE 2.4 FUNCTIONS $\text{E}^{-\text{AX}}$ (SYM1) AND $\text{XE}^{-\text{AX}}$ (SYM2).....56

FIGURE 2.5 MEASURED, FITTED AND RESIDUAL SPECTRUM FOR N₂O BETWEEN 2130 AND 2160 cm^{-1} , MICRO-WINDOW 1.62

FIGURE 2.6 MEASURED, FITTED AND RESIDUAL SPECTRUM FOR N₂O BETWEEN 2190.65 AND 2191.25 cm^{-1} , MICRO-WINDOW 38.62

FIGURE 2.7 WEIGHTS AS A FUNCTION OF MICRO-WINDOW FOR EACH N₂O ISOTOPOMER.....64

FIGURE 2.8 $\delta^{14}\text{N}^{15}\text{N}^{16}\text{O}$ DETERMINATIONS FOR CONSECUTIVE N₂O SPECTRA SERIES SE25033M DETERMINED WITH DIFFERENT SETS OF WEIGHTS.68

FIGURE 2.9 FLOWCHART FOR SPECTRAL ANALYSIS BY NON-LINEAR LEAST SQUARES BY THE PROGRAM NLM3.72

FIGURE 2.10 STANDARD ERROR SURFACE FOR $^{14}\text{N}^{15}\text{N}^{16}\text{O}$ ISOTOPOMER A FUNCTION OF UPPER AND LOWER EDGE OF THE NLM3 FIT WINDOW.....74

FIGURE 2.11 STANDARD ERROR SURFACE FOR $^{15}\text{N}^{14}\text{N}^{16}\text{O}$ ISOTOPOMER A FUNCTION OF UPPER AND LOWER EDGE OF THE NLM3 FIT WINDOW.....76

FIGURE 2.12 STANDARD ERROR SURFACE FOR $^{14}\text{N}^{14}\text{N}^{18}\text{O}$ ISOTOPOMER AS A FUNCTION OF UPPER AND LOWER EDGE OF THE NLM3 FIT WINDOW.....76

FIGURE 2.13 STANDARD ERROR SURFACE FOR $^{14}\text{N}^{14}\text{N}^{17}\text{O}$ ISOTOPOMER AS A FUNCTION OF UPPER AND LOWER EDGE OF THE NLM3 FIT WINDOW.....77

FIGURE 2.14 STANDARD ERROR SURFACE FOR PARENT $^{14}\text{N}^{14}\text{N}^{16}\text{O}$ ISOTOPOMER AS A FUNCTION OF UPPER AND LOWER EDGE OF THE NLM3 FIT WINDOW79

FIGURE 2.15	NON-LINEAR LEAST SQUARES FIT TO THE 2120 – 2270 cm^{-1} (LEFT) AND 2172.1–2172.6 cm^{-1} (RIGHT) REGIONS OF THE N_2O SPECTRUM.....	80
FIGURE 3.1	THE INFRARED OPTICAL CONFIGURATION.....	87
FIGURE 3.2	ENGINEERING DRAWING OF THE TEMPERATURE CONTROL SYSTEM AND WHITE CELL	88
FIGURE 3.3	SCHEMATIC DIAGRAM OF THE SAMPLE HANDLING MANIFOLD AND WHITE CELL	89
FIGURE 3.4	THE SAMPLE HANDLING MANIFOLD ATTACHED TO THE DA8 SPECTROMETER	90
FIGURE 3.5	DIFFERENCE BETWEEN FTIR AND IRMS MEASUREMENT OF THREE N_2O WORKING STANDARDS RELATIVE TO BOC GASES N_2O	98
FIGURE 4.1	PRECISION SURFACE FOR δ^{456} WITH VARIABLE N_2O AMOUNT AND SPECTRAL RESOLUTION FOR A CONSTANT 30 MINUTE ACQUISITION TIME AND VARIABLE SIGNAL TO NOISE RATIO.	105
FIGURE 4.2	CROSS SECTION OF PRECISION SURFACE (FIGURE 4.1) FOR 0.8 TORR N_2O	105
FIGURE 4.3	THEORETICAL DETERMINATION PRECISION FOR N_2O ISOTOPOMERS BY NON-LINEAR AND CLASSICAL LEAST SQUARES TECHNIQUES.	108
FIGURE 4.4	THE EFFECT OF A TEMPERATURE CHANGE ON PARTIAL PRESSURE DETERMINATION (LEFT) AND δ DETERMINATION (RIGHT) AS DETERMINED BY CLS	111
FIGURE 4.5	THE EFFECT OF A TEMPERATURE CHANGE ON PRESSURE DETERMINATION (LEFT) AND δ DETERMINATION (RIGHT) AS DETERMINED BY NLLS	112
FIGURE 4.6	THE EFFECT OF A PRESSURE CHANGE ON PRESSURE DETERMINATION (LEFT) AND δ DETERMINATION (RIGHT) AS DETERMINED BY CLS.....	115
FIGURE 4.7	THE EFFECT OF A PRESSURE CHANGE ON PRESSURE DETERMINATION (LEFT) AND δ DETERMINATION (RIGHT) AS DETERMINED BY NLLS	116
FIGURE 4.8	SINGLE SCAN REPRODUCIBILITY FOR HIGH RESOLUTION SPECTRA DETERMINED ON 25 SEPTEMBER 2000.	118
FIGURE 4.9	LINE SHAPE OF 25 CONSECUTIVE 30-SCAN SPECTRA.	119
FIGURE 5.1	RAYLEIGH DISTILLATION PLOTS FOR N_2O PHOTOLYSIS AT 211.5 NM, 207.6 NM AND 193 NM FOR ^{15}N ISOTOPOMERS.....	129
FIGURE 5.2	RAYLEIGH DISTILLATION PLOTS FOR N_2O PHOTOLYSIS AT 211.5 NM, 207.6 NM AND 193 NM FOR $^{14}\text{N}^{14}\text{N}^{18}\text{O}$ AND $^{14}\text{N}^{14}\text{N}^{17}\text{O}$ ISOTOPOMERS.....	130
FIGURE 5.3	COMPARISON OF ϵ^{456} AND ϵ^{546} ENRICHMENT FACTORS PREDICTED BY TWO N_2O PHOTOLYSIS THEORIES	134
FIGURE 5.4	ENRICHMENT FACTORS $\epsilon^{15}\text{N}$ AND $\epsilon^{456-546}$ FOR THE LABORATORY PHOTOLYSIS OF N_2O	135
FIGURE 5.5	ENRICHMENT FACTORS ϵ^{448} AND ϵ^{447} FOR THE LABORATORY PHOTOLYSIS OF N_2O	136
FIGURE 5.6	ENRICHMENT FACTOR RATIOS $\epsilon^{456}/\epsilon^{546}$ AND $\epsilon^{448}/\epsilon^{447}$ FOR THIS WORK AND TWO THEORIES	137
FIGURE 6.1	$\delta^{15}\text{N}$ AS A FUNCTION OF N_2O MIXING RATIO FOR THE COLLECTED TROPOSPHERIC N_2O SAMPLES	148
FIGURE 6.2	PERTURBATION OF AN N_2O RESERVOIR OF CONSTANT CONCENTRATION AND δ BY AN N_2O SOURCE (SCHEMATIC)	149
FIGURE 6.3	KEELING PLOT FOR $\delta^{15}\text{N}$ FOR COLLECTED TROPOSPHERIC N_2O SAMPLES	151

FIGURE 6.4	δ^{456} , δ^{546} AND δ^{456} - δ^{546} AS A FUNCTION OF N_2O MIXING RATIO	154
FIGURE 6.5	δ^{456} - δ^{546} AS A FUNCTION OF $\delta^{15}N$ (LEFT) AND δ^{546} (RIGHT) FOR THIS WORK AND <i>YOSHIDA AND TOYODA</i> [2000]	158
FIGURE 6.6	$\delta^{15}N$ (RIGHT) AND δ^{448} (LEFT) AS A FUNCTION OF RAIN FALL, 24 HOURS TO 0900.....	158
FIGURE 7.1	LOCATION OF COROWA, NSW.....	166
FIGURE 7.2	SCHEMATIC DIAGRAM OF THE COROWA EXPERIMENT SITE.	166
FIGURE 7.3	THE COROWA FIELD SITE, LOOKING EAST TOWARDS THE ACCESS ROAD	168
FIGURE 7.4	THE BOOM IRRIGATOR	168
FIGURE 7.5	THE WATERLOGGED REGION OF THE CROP FIELD SITE	169
FIGURE 7.6	THE N_2O EXTRACTION LINE MOUNTED INSIDE THE 4WD VEHICLE	169
FIGURE 7.7	RELATIVE RATES OF NITRIFICATION AND DENITRIFICATION AS A FUNCTION OF WATER FILLED PORE SPACE.	177
FIGURE 7.8	FLUX N_2O AS A FUNCTION OF TIME POST-IRRIGATION.....	179
FIGURE 7.9	$\delta^{15}N$ OF N_2O SOIL EMISSIONS AS A FUNCTION OF N_2O FLUX FOR COROWA FIELD SITES	179
FIGURE 7.10	$\delta^{15}N$ OF N_2O SOIL EMISSIONS AS A FUNCTION OF TIME POST-IRRIGATION FOR COROWA FIELD SITES	180
FIGURE 7.11	INTRAMOLECULAR ^{15}N DIFFERENCE (δ^{456} - δ^{546}) OF N_2O SOIL EMISSIONS AS A FUNCTION OF N_2O FLUX FOR COROWA FIELD SITES	184
FIGURE 7.12	δ^{546} AS A FUNCTION OF δ^{456} FOR THE COROWA FIELD SITES.	184
FIGURE 7.13	δ^{456} - δ^{546} AS A FUNCTION OF $\delta^{15}N$ FOR THIS WORK, <i>PEREZ ET AL.</i> [2001] AND <i>MENEGAZZO</i> [2000].	187
FIGURE 7.14	δ^{448} RELATIVE TO ATMOSPHERIC O_2 FOR N_2O SOIL EMISSIONS AS A FUNCTION OF N_2O FLUX (LEFT) AND TIME POST-IRRIGATION (RIGHT) FOR COROWA FIELD SITES.....	189
FIGURE 7.15	δ^{447} FOR N_2O SOIL EMISSIONS AS A FUNCTION OF N_2O FLUX (LEFT) AND TIME POST-IRRIGATION (RIGHT) FOR COROWA FIELD SITES.....	189
FIGURE 7.16	δ^{448} (REL. ATM. O_2) AS A FUNCTION OF $\delta^{15}N$ (REL. ATM. N_2) FOR THIS WORK, <i>PEREZ ET AL.</i> [2001] AND <i>MENEGAZZO</i> [2000].	190
FIGURE 7.17	δ^{447} AS A FUNCTION OF δ^{448} FOR COROWA FIELD SITES	191
FIGURE 7.18	$\Delta^{17}O$ FOR N_2O SOIL EMISSIONS AS A FUNCTION OF N_2O FLUX (LEFT) AND TIME POST-IRRIGATION (RIGHT) FOR COROWA FIELD SITES.....	192

LIST OF TABLES

TABLE 1.1	GLOBAL WARMING POTENTIALS FOR SEVERAL GREENHOUSE GASES ^(A)	4
TABLE 1.2	SOURCE AND SINK ESTIMATES FOR N ₂ O	8
TABLE 1.3	ISOTOPOMERS OF N ₂ O AND THEIR NATURAL ABUNDANCES	15
TABLE 2.1	MICRO-WINDOWS USED IN CLS ANALYSIS OF HIGH RESOLUTION N ₂ O SPECTRA	60
TABLE 2.2	NUMBER OF MICRO-WINDOWS CONTRIBUTING 90% OF TOTAL WEIGHT IN MICRO-WINDOW CLS ANALYSIS.....	63
TABLE 2.3	STANDARD DEVIATION OF ISOTOPOMER DETERMINATION FOR A SERIES OF SPECTRA ^(A) DETERMINED BY NLLS AND CLS TECHNIQUES.....	81
TABLE 3.1	RELATIVE ISOTOPIC SIGNATURES OF VARIOUS N ₂ O WORKING STANDARDS DETERMINED BY THE FTIR METHOD	97
TABLE 3.2	δ ¹⁵ N AND δ ¹⁸ O OF N ₂ O WORKING STANDARDS RELATIVE TO ATMOSPHERIC N ₂ AND O ₂ , RESPECTIVELY *	99
TABLE 4.1	CONDITIONS USED FOR ESTIMATING THE ISOTOPOMER PRECISION SURFACE	104
TABLE 4.2	THEORETICAL DETERMINATION PRECISION AT RMS-SNR 1000 AND BEST EXPERIMENTAL PRECISION.	109
TABLE 4.3	COMPARATIVE ISOTOPIC DETERMINATION PRECISIONS (± 1 σ) FOR TWO FTIR SPECTROMETERS	120
TABLE 4.4	THE STANDARD SPECTROSCOPIC CONDITIONS	121
TABLE 4.5	THE STANDARD SPECTRAL ANALYSIS CONDITIONS	122
TABLE 4.6	PERFORMANCE SUMMARY FOR THE FTIR METHOD.....	122
TABLE 5.1	ISOTOPOMER DETERMINATIONS IN PER MILLE RELATIVE TO SNOW ^(A) FOR LABORATORY PHOTOLYSED N ₂ O BY NON-LINEAR LEAST SQUARES	128
TABLE 5.2	PHOTOLYSIS ENRICHMENT FACTORS OF N ₂ O DETERMINED BY NON-LINEAR LEAST SQUARES	131
TABLE 5.3	PHOTOLYSIS ENRICHMENT ACTORS OF N ₂ O DETERMINED BY CLS FOR THIS EXPERIMENT AND PREVIOUSLY PUBLISHED BY <i>TURATTI ET AL.</i> [2000].....	131
TABLE 6.1	LOCAL SCALE WEATHER CONDITIONS FOR EACH N ₂ O SAMPLE COLLECTION.....	144
TABLE 6.2	MIXING RATIOS OF N ₂ O, CO ₂ , CH ₄ AND CO FOR COLLECTED TROPOSPHERIC AIR SAMPLES	145
TABLE 6.3	ISOTOPOMER RESULTS ^(A) FOR TROPOSPHERIC N ₂ O SAMPLES COLLECTED FROM WOLLONGONG, AUSTRALIA	147
TABLE 6.4	ANALYSIS OF CLEAN BACKGROUND AIR FROM CAPE SHANK, VICTORIA	152
TABLE 7.1	FLUXES OF N ₂ O AND CO ₂ FOR THE COROWA FIELD EXPERIMENT SITES.....	173
TABLE 7.2	N ₂ O ISOTOPIC SIGNATURES FOR COROWA FIELD EXPERIMENT SITES ^(A)	174